

# Recovering Metallicity in $A_4C_{60}$ : The Case of Monomeric $Li_4C_{60}$

M. Riccò,\* M. Belli, D. Pontiroli, M. Mazzani, and T. Shiroka

*Dipartimento di Fisica and Consorzio Nazionale Interuniversitario per le Scienze Fisiche della Materia,  
Università di Parma, Via G. Usberti 7/a, 43100 Parma, Italy*

D. Arčon and A. Zorko

*Solid State Physics Department, Jozef Stefan Institute, Jamova 39, SI-1000, Ljubljana, Slovenia*

S. Margadonna

*School of Chemistry, University of Edinburgh, West Mains Road, EH9 3JJ Edinburgh, UK*

G. Ruani

*ISMN-CNR, Via P. Gobetti 101, 40129 Bologna, Italy*

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The restoration of metallicity in the high-temperature, cubic phase of  $Li_4C_{60}$  represents a remarkable feature for a member of the  $A_4C_{60}$  family ( $A$  = alkali metal), invariably found to be insulators. Structural and resonance technique investigations on  $Li_4C_{60}$  at  $T \lesssim 600$  K, show that its fcc structure is associated with a complete ( $4e^-$ ) charge transfer to  $C_{60}$  and a sparsely populated Fermi level. These findings not only emphasize the crucial role played by lattice symmetry in fulleride transport properties, but also re-dimension the role of Jahn-Teller effects in band structure determination.

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In recent years the competition between Coulomb repulsion, kinetic energy, Jahn-Teller effect, and Hund's coupling rules has been subject of intensive research in the domain of alkali-doped fullerenes. Apparently, most of the phenomena, including high- $T_c$  superconductivity in  $A_3C_{60}$ , seem to be relatively well understood. Nevertheless, the reason why  $A_4C_{60}$  are in general nonmagnetic insulators [1, 2] is still puzzling and remains subject of strong controversy. The situation is made even more complex as, differently from fcc  $A_3C_{60}$ , the  $A_4C_{60}$  arising from large-size alkali metals ( $A$  = K, Rb, Cs) adopt a bct structure [3]. Hence, the natural suggestion that the difference in lattice structure favors the metallicity in the former and an insulating behavior in the latter, with the coupling to  $H_g$  Jahn-Teller phonons accounting for the lack of magnetic ordering in  $A_4C_{60}$ [4].

Doping the  $C_{60}$  with the significantly smaller  $Li^+$  and  $Na^+$  alkali ions leads to interesting deviations from the standard behavior. Indeed,  $Li_xC_{60}$  can easily form compounds with  $x > 6$  [5], whereas in  $Na_4C_{60}$  the fullerene molecules form a 2D planar polymer, with the molecular units linked by four single C–C bonds [6]. As commonly observed in singly bonded  $C_{60}$  polymers [7], the latter system too was reported to be metallic [6, 8].  $Li_4C_{60}$ , though, represents a different situation. At normal conditions, it is a 2D polymer displaying a novel architecture based on the coexistence of single and double bonds oriented along two perpendicular directions within the polymer plane [9]. Although the presence of single bonds could suggest a metallic behavior, NMR, Raman and ESR spectroscopy show beyond doubt the diamagnetic and insulating character of this polymer [10]. Important

questions hence arise both regarding the role of structure, as well as of polymerization in depressing the electron delocalization and destroying the expected metallicity.

In this article we try to answer these questions by a thorough investigation of the high temperature monomeric  $Li_4C_{60}$  phase, obtained by thermally induced depolymerization which takes place above 590K. First we show that, in spite of its stoichiometry, the  $Li_4C_{60}$  monomeric phase retains a closed packed (fcc) cubic structure, and therefore can be directly compared to other, well known  $A_3C_{60}$  fcc systems. Subsequently, as revealed from the ESR lineshape,  $^7Li$  and  $^{13}C$  NMR Knight shift and Raman bandwidth, we demonstrate the metallicity of the monomeric  $Li_4C_{60}$ . Finally, a full charge transfer of four electrons to  $C_{60}$  is clearly evidenced by the Raman  $A_g(2)$  mode shift. These results not only challenge established theories on alkali intercalated fullerenes, but also stimulate a re-consideration of the relative importance of the many competing mechanisms present in these systems.

The  $Li_4C_{60}$  samples were prepared following intercalation procedures described in detail elsewhere [10]. High-resolution synchrotron X-ray powder diffraction data on  $Li_4C_{60}$  were collected on the ID31 beamline at the ESRF facility (Grenoble) at 773 K ( $\lambda = 0.85055$  Å), well above the depolymerization temperature ( $T_{dep} \sim 590$  K) (Fig. 1). The rebinned data were then analyzed using the Fullprof suite of Rietveld analysis programs.

All the peaks of the powder diffraction profile were indexed with a face centered cubic cell, except for an evident shoulder at  $2\theta \sim 6^\circ$  on the leftmost peak, present also in pristine cubic  $C_{60}$  and generally associated to

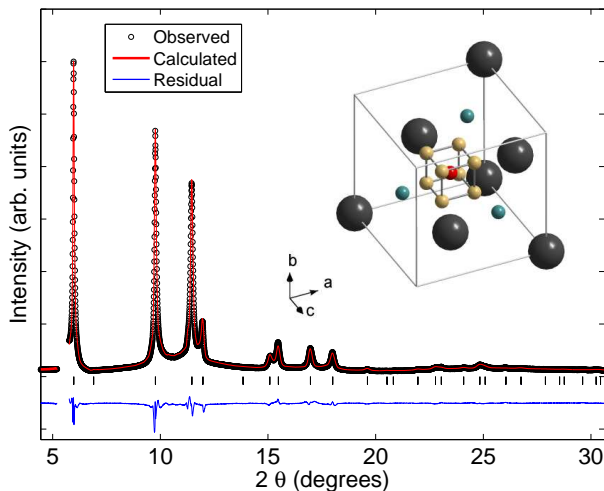


FIG. 1: (color online). Calculated and observed synchrotron powder diffraction profile of  $\text{Li}_4\text{C}_{60}$  at 773 K, taken with  $\lambda = 0.85055 \text{ \AA}$  ( $R_{\text{wp}} = 4.04\%$ ,  $R_{\text{exp}} = 2.96\%$ ). Inset: crystal structure of  $\text{Li}_4\text{C}_{60}$  monomer. Lithium atoms (small spheres) occupy three different non-equivalent positions in the fcc lattice ( $a = 14.122 \text{ \AA}$ ) formed by fullerene units (large spheres).

stacking faults among the (111) planes [11].

Starting with a face centered cubic structure (space group  $Fm\bar{3}m$ ), data analysis using the Le Bail pattern decomposition technique proceeded smoothly, resulting in a lattice parameter  $a = 14.122 \text{ \AA}$  (agreement factors:  $R_{\text{wp}} = 3.33\%$ ,  $R_{\text{exp}} = 2.44\%$ ). It is worth noting that the  $\sim 9.97 \text{ \AA}$  inter-ball distance between two nearest  $\text{C}_{60}$  units, although slightly smaller than in pristine  $\text{C}_{60}$  (due to positive electrostatic pressure), is fully compatible with that in monomeric fullerenes.

To account for the orientational disorder in the high temperature phase, during Rietveld refinement the fullerene units were modeled with quasi-spherical shells centered at  $4a(0, 0, 0)$  sites. Their scattering density was described in terms of symmetry-adapted spherical harmonics (SASH) which, compatibly with the symmetry of the system, comprise only  $K_{l,j}(\theta, \phi)$  terms with  $l = 0, 6, 10$ . The respective coefficients  $c_{l,j}$ , treated as free refinement parameters, have fitted values  $c_{6,1} = 0.035(3)$  and  $c_{10,1} = -0.156(13)$ . The latter is indicative of an excess electronic density along the  $[111]$  directions, where tetrahedral lithium ions are expected to reside. Nevertheless, the relatively small value of the  $c_{10,1}$  coefficient (to be compared with  $c_{10,1} = -0.26(3)$  in  $\text{Li}_2\text{CsC}_{60}$  [12]) suggests a considerably weakened  $\text{Li}^+-\text{C}$  interaction.

While three of the intercalated lithium ions were easily localized in the octahedral ( $4b$ ) and the two tetrahedral ( $8c$ ) sites, the location of the fourth excess  $\text{Li}^+$  proved a more difficult task. A difference Fourier analysis revealed the existence of scattered intensity in the vicinity of the  $32f$  sites ( $x, x, x$ , with  $x \sim 0.375$ ), which define a cube centered at the  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  cell position. Subsequent Ri-

etveld refinements, repeated after introducing the missing  $\text{Li}^+$  ion in these sites and allowing for its occupation number to vary, indicated that the excess alkali ion is randomly distributed over the corners of the cube with  $\frac{1}{8}$  occupancy.

The proposed structure (see inset in Fig. 1) shows deep analogies with another cubic fulleride,  $\text{Li}_3\text{CsC}_{60}$  [13], which presents similar stoichiometry, but only a partial charge transfer of 3 electrons [14]. The accurate evaluation of  $\text{Li}^+-\text{C}$  contact distances ( $\sim 2.4 \text{ \AA}$ ) confirmed once more their weak mutual interactions, strongly suggesting an almost *complete* charge transfer from the intercalated metal to the  $\text{C}_{60}$  units. Hence, the structural analysis not only shows that the high-temperature treatment of the 2D polymeric  $\text{Li}_4\text{C}_{60}$  leads to a fcc monomeric phase, analogous to those observed in  $\text{A}_3\text{C}_{60}$ , but it gives also precise, though indirect, hints about the electronic properties, whose direct investigation is described in detail below.

A straightforward evidence about the metallic character of the  $\text{Li}_4\text{C}_{60}$  monomer is given by the presence of a Knight shift in Nuclear Magnetic Resonance (NMR) spectra of both  $^{13}\text{C}$  and  $^7\text{Li}$  nuclei. The room temperature  $^{13}\text{C}$  NMR spectrum of the as-prepared  $\text{Li}_4\text{C}_{60}$  polymer confirms the insulating nature of the compound [10], whereas heating the sample to high temperatures introduces significant spectral changes. The nearly structureless spectrum measured at  $T = 673 \text{ K}$  (Fig. 2), well above the depolymerization transition, is fully compatible with freely rotating  $\text{C}_{60}$  molecules, as expected in a monomeric phase. What we find really surprising is the considerable positive shift of the  $^{13}\text{C}$  NMR line,  $\delta\nu = 195 \text{ ppm}$ , much larger than typical values reported for metallic  $\text{A}_3\text{C}_{60}$  fullerenes [15]. This fact clearly suggests an increased value of the isotropic Knight shift and could be rationalized in the same framework of the ESR results (*vide infra*) by a substantial increase of the isotropic hyperfine coupling for the  $\text{C}_{60}^{4-}$  state, as compared to the one measured for  $\text{C}_{60}^{3-}$ .

The  $^7\text{Li}$  NMR spectrum of the monomer phase of  $\text{Li}_4\text{C}_{60}$ , reported in Fig. 2(b), shows two partially merged peaks centered at  $+28$  and  $+48 \text{ ppm}$  relative to  $\text{LiCl}$ . They comprise all of the transitions of the  $^7\text{Li}$  nucleus ( $I = \frac{3}{2}$ ), as confirmed by nutation angle analysis. The upshift can easily be attributed to a metallic behavior, since typical shifts in other, insulating lithium fullerides would fall in the few ppm range [5, 10, 16]. It seems to follow quite well the common trend of metallic fullerides, where smaller alkali metals give rise to lower shift values [17].

Even though the non-negligible temperature dependence of the relative intensities prevented us from a detailed analysis, we may still attribute the more shifted peak to the disordered lithium ions in the  $32f$  sites, as a higher electronic density is expected at these asymmetric positions, due to a theoretically predicted enhancement

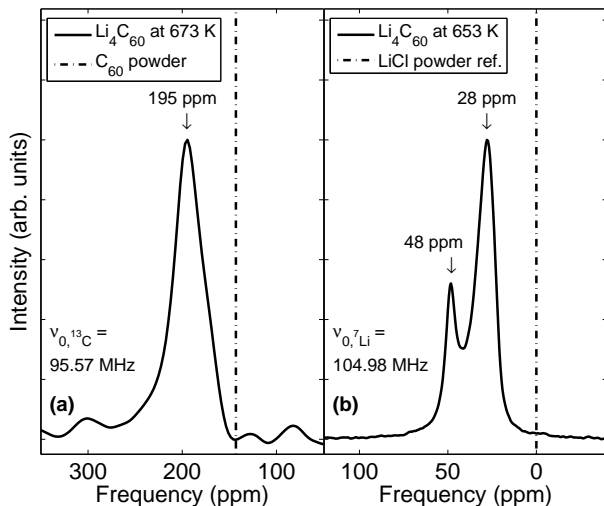


FIG. 2: NMR spectra of  $\text{Li}_4\text{C}_{60}$  in the monomer phase: (a)  $^{13}\text{C}$  NMR spectrum at 673 K referenced to tetramethyl silane. The pristine  $\text{C}_{60}$  line position at +143 ppm is also shown by dotted line; (b)  $^7\text{Li}$  spectrum at 653 K referenced to the narrow line of anhydrous  $\text{LiCl}$  powder measured at the same temperature.

of the fullerene–alkali metal electronic hopping [18].

Further evidence on the metallic ground state of the high-temperature phase comes from ESR experiments. At room temperature, the as-prepared polymeric  $\text{Li}_4\text{C}_{60}$  displays an extremely narrow X-band ESR signal ( $\Delta H_{pp} = 0.27(3)$  G), described quite well by a simple Lorentzian lineshape. The calibrated ESR signal intensity corresponds to a small spin susceptibility,  $0.24 \times 10^{-4}$  emu/mol, and to a  $g$ -factor insignificantly larger than 2. As the sample is heated, the ESR signal undergoes dramatic changes. Indeed, already at 370 K, the lineshape becomes slightly anisotropic, whereas for temperatures above 520 K the anisotropy becomes extremely pronounced (see inset in Fig. 3). The lineshape closely resembles a Dysonian function [19], providing a clearcut indication of the metallic character of the monomer.

In parallel with lineshape evolution, signal intensity too shows a sudden increase by nearly an order of magnitude and, at  $T = 620$  K, the ESR spin susceptibility reaches  $\chi_S = 1.3(2) \cdot 10^{-4}$  emu/mol, a value comparable with those measured in monomeric metallic  $\text{A}_x\text{C}_{60}$  [20]. We would like to stress that, despite the increase, this value remains nevertheless smaller than any other known spin susceptibility in metallic  $\text{C}_{60}$  phases. In fact, the measured Pauli susceptibility  $\chi_S$  implies a density of states at the Fermi level  $N(E_F) \sim 5$  states/eV, to be compared with  $N(E_F) \sim 14$  states/eV obtained in a typical  $\text{A}_3\text{C}_{60}$  compound with similar lattice parameter [21].

This reduction in the density of states could arise either from an increased bandwidth  $W$ , or from strong spin correlation effects. An increase in bandwidth up to 40%

TABLE I: Fitted parameters for  $\text{Li}_4\text{C}_{60}$  and pristine  $\text{C}_{60}$  Raman spectra taken at 648 K. The line shifts  $\omega_0$  and widths  $\Gamma$  are expressed in  $\text{cm}^{-1}$ , the Fano parameter  $q$  is adimensional.

		$H_g(1)$	$H_g(2)$	$A_g(1)$	$A_g(2)$
$\text{Li}_4\text{C}_{60}$ :	$\omega_0$	279.5(7)	422.5(4)	503.3(2)	1431.1(2)
	$\Gamma$	21(1)	21.0(6)	8.0(5)	19.2(5)
	$q$	-8(2)	-7(1)	—	—
$\text{C}_{60}$ :	$\omega_0$	275.9(1)	— <sup>a</sup>	497.6(1)	1458.8(2)
	$\Gamma$	5.8(5)	— <sup>a</sup>	3.5(3)	5.6(7)

<sup>a</sup> $H_g(2)$  mode in pristine  $\text{C}_{60}$  not detectable at this temperature.

[18] is already expected in bct  $\text{A}_4\text{C}_{60}$  systems, due to the presence of alkali ions in non-symmetric positions. In our case, the same effect could arise from the Li ions located in the  $32f$  sites. If this were the case, not only the Pauli susceptibility would be reduced, but also the effective ESR  $g$ -factor would be affected. As a comparison, typical  $g$ -factor values in  $\text{Rb}_3\text{C}_{60}$  and  $\text{K}_3\text{C}_{60}$  are 1.9945 and 2.0003 respectively [20], whereas in the high-temperature fcc phase of  $\text{Li}_4\text{C}_{60}$  we find  $g = 2.0036(5)$ , a value strikingly different from the others. Such an anomalously high  $g$ -factor could reflect either an enhanced  $\text{C}_{60}$ –Li electron hopping mechanism or continuous changes in the spin-orbit scattering due to lithium disorder in  $\text{Li}_4\text{C}_{60}$ .

Raman spectra were recorded in a back-scattering geometry from room temperature up to 648 K. A relatively low laser intensity ( $200 \text{ W/cm}^2$ ) helped us to avoid the photo-damage of the investigated samples. The room temperature Raman scattering is characterized by a large number of narrow lines, typical of an insulating, low-symmetry polymer [10]. On the other hand, at high temperatures most of the peaks disappear and only four of them (Fig. 3), attributed to the  $H_g(1)$ ,  $H_g(2)$ ,  $A_g(1)$  and  $A_g(2)$  modes, could be observed. While the  $A_g$  modes are symmetric and could be fitted to Lorentzian peaks, the  $H_g$  modes display an asymmetric shape and were thus analyzed in terms of Breit-Wigner-Fano (BWF) resonances [22]; the best fit values are reported in Tab. I. The spectrum is very similar to the one observed in  $\text{A}_3\text{C}_{60}$  ( $\text{A} = \text{K}, \text{Rb}$ ) ([23] and refs. therein), once more confirming the metallic nature of the compound.

To determine the charge transfer towards  $\text{C}_{60}$  we use the well known fact that  $A_g(2)$  mode energy shifts are proportional to the number of transferred electrons ( $6\text{--}7 \text{ cm}^{-1}/\text{electron}$  [24]). However, to discriminate purely thermal effects from alkali doping, we perform (at the same temperature) a comparative Raman scattering in undoped  $\text{C}_{60}$ , whose modes could be fitted with Lorentzian curves (see Tab. I).

The doping-related energy shift of the  $A_g(2)$  mode,  $27.8 \text{ cm}^{-1}$ , is consistent with a charge transfer of four electrons per  $\text{C}_{60}$  ( $6.9 \text{ cm}^{-1}/\text{electron}$ ). Finally, the presence of BWF line shapes indicates an interaction of the  $H_g$  modes with free electrons in the  $t_{1u}$ -derived state of

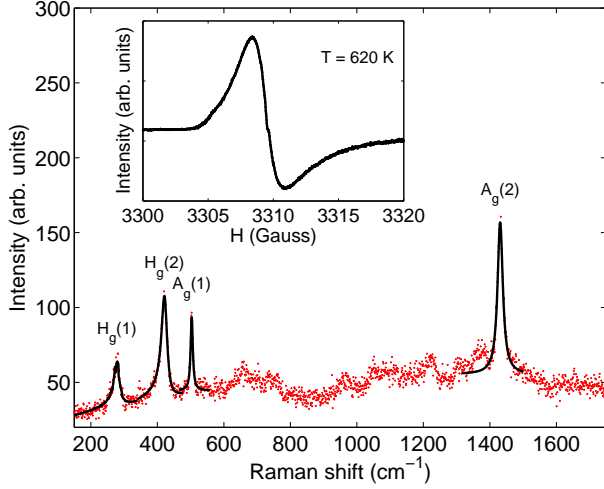


FIG. 3: (color online). Raman spectrum of monomeric  $\text{Li}_4\text{C}_{60}$  (dots) taken at 648 K with a 1.96 eV excitation. Only four Raman modes, associated to  $A_g$  and  $H_g$  cage vibrations, are clearly detected and respectively fitted to Lorentzian and BWF curves (solid lines). The  $H_g$  resonances appear broadened and asymmetric, in agreement with the metallic nature of the compound. Inset: The anisotropic Dysonian lineshape of the ESR signal at 620 K also supports the sample's metallicity.

$\text{C}_{60}$  molecule. From the phonon frequency  $\omega_i$  and the full width at half maximum  $\Gamma_i$  of the  $i^{\text{th}}$  mode, one can estimate the electron-phonon coupling constants  $\lambda_i$  ([25] and refs. therein):

$$\lambda_i = \frac{d_i \Gamma_i}{\pi \omega_i^2} \frac{2}{N(E_F)}, \quad (1)$$

where  $d_i$  is the degeneracy of the mode. By assuming a density of states at the Fermi level  $N(E_F) \sim 5$  states/eV, as deduced from ESR, and using the fitted parameters in Tab. I, we obtain the relatively high  $\lambda_{H_g(1)} = 1.4$  and  $\lambda_{H_g(2)} = 0.6$ , whereas the contribution from the  $A_g$  modes is completely negligible.

In conclusion, we have shown that an  $\text{A}_4\text{C}_{60}$  fulleride which assumes an fcc structure is metallic. Although there are already some indications that  $\text{A}_4\text{C}_{60}$  fullerides are on the verge of a metal-to-insulator transition (MIT) ( $\text{Rb}_4\text{C}_{60}$  at high pressure [26], tetragonal  $\text{Na}_4\text{C}_{60}$  [27]), the metallicity is not a direct consequence of the lattice contraction due to the small dimension of the intercalated ions. Indeed,  $\text{K}_4\text{C}_{60}$  presents the same inter-ball distance as  $\text{Li}_4\text{C}_{60}$ , but it is an insulator. This indicates that lattice symmetry plays a dominant role [4], unlike molecular effects such as Jahn-Teller distortions, which tend to stabilize an insulator [28]. Compared to super-

conducting  $\text{A}_3\text{C}_{60}$ , this system has a broader bandwidth (probably related to the presence of asymmetric Li ions), but a relatively stronger electron-phonon coupling. This suggests that a moderate lattice expansion (achieved, for example, by the co-intercalation of small molecules like ammonia [29]) would preserve the metallic state, while inhibiting the formation of a polymer at low temperatures. Such a new material is very likely to show high- $T_c$  superconductivity.

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\* Electronic address: Mauro.Ricco@fis.unipr.it

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